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OZONE AND ANTOZONE. *see Cat.*

BY CHARLES M. WETHERILL, PH. D., M. D.

SCHOENBEIN, in the year 1840, called attention to the existence of a substance which he named from one of its most striking characteristics, ozone, (*οζω, I smell.*) The peculiar odor in the neighborhood of a good electrical machine when in action, and especially when the electricity issues from a point upon the prime conductor, or is drawn from it as a spark, had been well known. A similar odor had also been perceived accompanying the fall of the thunderbolt.* This phenomenon had been characterized as a phosphoric or a sulphur smell.

Schoenbein called attention to the fact that a similar smell is perceived during the decomposition of water by the voltaic pile, and is observed accompanying the oxygen which appears at the positive pole when the gases are collected separately, and that it is also experienced in many chemical processes, especially in those involving a slow combustion. In explaining the odor of the active electrical machine, it had been assumed that the sensation is due solely to a peculiar action of the electricity upon the organs of smell, and not to the presence of a material substance; but Schoenbein discovered, in the cases alluded to, the existence of a body having the chemical properties of active oxygen—that is, of this gas in its condition of entering most readily into chemical combination, to which he attributed the phenomenon in question, and to which he assigned a characteristic name.

During the twenty-five years which have elapsed since Schoenbein's discovery, this difficult subject has been investigated by many scientists, and especially by Schoenbein himself, by Marignac, De la Rive, Fremy, Erdmann, Berzelius, Williamson, Becquerel, Baumert, and others equally well known in research. While there are few subjects which present a wider field for investigation, or which are more important in their relations to a knowledge of animal life, and to some interesting practical questions in technology, there are few which require a greater patience, or a greater degree of skill in manipulation for their research. It is in consequence of these difficulties that our knowledge of ozone is so limited, notwithstanding the time and labor which have been bestowed upon it. It is the object of the present article to give a brief sketch of what is known respecting this substance, on the authority of the article ozone in Poggendorff's Dictionary, and from the essays of experimentors in various scientific periodicals.

Some time elapsed after its discovery before very definite views were held as to the true nature of ozone. Schoenbein, who for a long time denied that ozone is an allotropic form of oxygen, at first supposed that it was a new body which, in union with oxygen, or perhaps with hydrogen, constituted nitrogen, to which he attributed a compound character. De la Rive imagined that the peculiar smell was due to the action upon the organ, of

* Homer notices the smell of the thunderbolt. Mohr in Pogg. Ann., xci, 625. Thus, in the Odyssey, book xii, verse 417, and xiv, 307, Jupiter strikes a ship with a thunderbolt, *εν δε θεειον πληρο*, "quite full of sulphurous odor." In the Illiad, viii, 135, Jove hurls a bolt, "with the flame of the burning sulphur," into the ground before Diomedes's chariot. In the same poem, xiv, 415, Ajax hurls a rock at Hector, who falls "like a mountain oak struck by lightning, which lies uprooted, and from which the fearful smell (*οδυν*) of smoking sulphur rises."



very finely divided metallic dust of platinum, or of gold, which was separated from the conductors by the electric current, and converted into oxides of the metals; but Schoenbein proved this explanation to be untenable by the experiment of employing hot points for the issuing of the electric charge into the air. Under such circumstances the hypothetical separation of metallic particles and their oxidation should be increased; but, upon the contrary, there was no smell of ozone at all perceptible. Besides this, ozonized air, when shaken in a bottle with water, does not lose its peculiar smell. Hence it is a gas, not absorbable by water, but altered in its character by heat. Marignac and De la Rive subsequently performed experiments which seemed to show that ozone is pure oxygen. As Marignac was unable to obtain ozone by electricity with oxygen unless moisture was present, it was possible that the substance might be peroxide of hydrogen, and this hypothesis became highly probable by the extended and careful research upon this point by Dr. Williamson. This chemist prepared ozone by the electrolysis of sulphate of copper, dried it by passage over chloride of calcium, and passed it through a tube containing copper turnings, heated to redness, which had been first oxidized and then reduced in a current of carbonic oxide. By the experiment, oxide of copper and water resulted. Schoenbein now adopted this hypothesis, having been fortified by experiments of his own. At first he regarded ozone as a higher oxide (HO_3) than Thenard's peroxide (HO_2) of hydrogen; but at last retained the latter formula. Schoenbein defended this view pertinaciously, supporting it by experiments and by arguments against that of De la Rive, Marignac, Marchand, Erdmann, Berzelius, Fremy, and Becquerel, who prepared ozone with pure oxygen, (obtained from chlorate of potassa, the gas being washed and perfectly dried,) either by the electrical machine or by an induction current. Marignac, by acting with ozone upon pure powder of metallic silver, obtained nothing but the peroxide of that metal. Hence the conclusion was warranted that ozone is oxygen in an allotropic form. Schoenbein's opinion was based upon his view of the halogen bodies, which, like Berthollet, he believed to be peroxides of unknown radicals, and from the analogy of ozone, in its chemical behavior, to chlorine. He also assumed that no *element* is known which has an action upon the olfactory nerves to call forth the sensation of smell; chlorine, iodine, and bromine being, as he believes, compounds, while phosphorus and arsenic act upon this sense by reason of their passage into the condition of oxides.

Baumert contended that the odorous gas evolved by electrolytic action is essentially different from ozone obtained by the electric spark. Its constitution, according to this chemist, is HO_3 ; it yields no water to anhydrous phosphoric acid until it has first passed through a tube heated to redness, which he supposed decomposes the HO_3 . Baumert, however, in subsequent experiments, acceded to the opinion (derived from their investigations) of De la Rive, Erdmann, Marignac, Marchand, Fremy, and Becquerel, that ozone is an allotropic condition of oxygen.

Schoenbein, in 1858, discovered that if to diluted peroxide of hydrogen a few drops of solution of acetate of lead be added, or that if ozonized oil of turpentine be shaken with the same lead salt, peroxide of lead is formed. The same reaction takes place when ozonized oxygen acts upon basic acetate of lead. When the peroxide of lead thus formed remains in contact with the peroxide of hydrogen, both are reduced; the result being water, protoxide of lead, and oxygen. From this reaction, Schoenbein assumed that the oxygen in the peroxides of hydrogen and of lead exists in an opposite condition of polarity, thus:

HO^+O and PbO^-O , and that by the union of these molecules of oxygen the ordinary inactive oxygen results. Clausius and De la Rive also imagined a similar molecular condition for oxygen.

Schoenbein designated those bodies containing negatively active oxygen, ($\bar{O}$), *ozonides*; such are permanganic ($Mn_2O_2\bar{O}_5$) and chromic acids ($Cr_2O_3\bar{O}_3$), and the peroxides of manganese, ($MnO\bar{O}$), silver, ($AgO\bar{O}$), and lead, ($PbO\bar{O}$). He named *antozonides*; peroxides of hydrogen, ($HO\bar{O}$), barium, ($BaO\bar{O}$), and all bodies which contain oxygen in a positively* active condition, ($\bar{O}$), and this form of oxygen he called *antozone*.

This chemist succeeded in obtaining antozone ($\bar{O}$) by projecting finely powdered peroxide of barium ($BaO\bar{O}$) into cold monohydrated sulphuric acid. A gas is evolved which both Houszeau and Schoenbein formerly supposed to be ozone, but which has different properties. It blues iodide of potassium starch paper, and smells somewhat like ozone; but when agitated with a little water it loses its odor completely, and forms peroxide of hydrogen, which reaction ozone does not produce. A slip of filter-paper saturated with a mixture of dilute solution of ferricyanide of potassium and a persalt of iron is *speedily* turned blue in antozone gas, but in ozone behaves as in atmospheric air. A very small portion of the gas evolved by this reaction in antozone. This is due to the elevation of temperature, which transforms the antozone into ordinary oxygen.

Another means of distinguishing ozone from antozone consists in a slip of paper imbued with solution of sulphate of protoxide of manganese, which speedily becomes brown in ozone, from the formation of peroxide of manganese. In antozone, not only does this reaction not take place, *but papers browned by ozone are bleached by antozone*.

A distinguishing test may also be found in the behavior of the two gases with permanganic acid, which antozone decolorizes and ozone browns.

Dr. G. Meissner discovered that, if well dried electrified air be passed through water, (which may or may not contain air,) it forms, upon issuing into the atmosphere, a more or less dense cloud or mist. The same phenomenon takes place when electrified air issues into a moist atmosphere.

This cloud is formed by the electrifying of either pure oxygen or of air; but not by pure hydrogen, or nitrogen. It occurs, whether the gas contains ozone or not, but in the latter case to a less degree.

By contact with drying substances, as concentrated sulphuric acid, chloride of calcium, and even concentrated solutions of certain salts, the mist may be caused to disappear; but it forms again by the addition of aqueous vapor. The air left to itself gradually loses this mist-producing property, and if the antozone cloud be confined, the water is, after a while, precipitated upon the sides of the vessel, and can no more be produced by the action of vapor, unless the air be electrified again.

Ozoniferous moist air retains its cloud-compelling property longer than that which does not contain ozone; and, on the other hand, *dry* ozonized air preserves this property still longer. Meissner satisfied himself, by numerous experiments, that this phenomenon of mist is due to antozone, and that electrified air contains both ozone and antozone, the former element being absorbed, and the latter not absorbable by iodide of potassium, or pyrogallic acid. He discovered, also, that antozone prepared by electricity is identical with that obtained by the decomposition of peroxide of barium, as the former, when brought fresh and dry in contact with water, generates a proportion of peroxide of hydrogen. Meissner regards peroxide of hydrogen as a chemical compound of antozone and water; but cloud or mist as a physical aggregate of antozone and vapor of water, in which the chemical affinity of the two bodies is very much weakened. Von Babo supposes the antozone cloud to be in most cases peroxide of

hydrogen, and that it may be formed by the action of ozone also; its disappearance he explains by the gradual precipitation, or decomposition of the peroxide.

Meissner regards the formation of ozone and antozone possible simultaneously by the action of either positive or negative electricity upon ordinary oxygen; but Von Babo believes that only ozone is formed by the current. The latter chemist found that ozonized air experienced no diminution of ozone upon its passage through a solution of permanganic acid, but that this took place immediately if the air came first in contact with substances capable of forming peroxide of hydrogen; also, that ozonized oxygen, free from nitrogen, generated with water neither cloud nor peroxide of hydrogen.

According to Meissner, antozone is formed by all processes of oxidation and combustion in oxygen; and, since the ozone enters chiefly, during combustion, into the oxide thus generated, that the result is principally antozone (or peroxide of hydrogen) in the free state. Antozone is, therefore, according to Meissner, the cause of the cloud in tobacco smoke, the smoke of chimneys, of gunpowder, fogs, and aerial clouds. Meissner found that the fumes of phosphorus in the air are *antozone* clouds, and not nitrate of ammonia, the greater portion of the *ozone* generated by the reaction being absorbed by the phosphorus.

Meissner discovered that air saturated with moisture gives a cloud, upon sudden rarefaction, until the barometric pressure is reduced to eight inches. This corresponds to an elevation of 27,000 feet. By the observations of Kämtz, the average altitude of the lightest and highest clouds, the cirrhi, is 20,000 feet, and their greatest height 24,000 feet.

According to Meissner, water condensed from air or oxygen has the form of *vesicles*, while, when it is separated from other gases, the moisture condenses in the form of *rain* or *solid drops*.

A most curious occurrence of antozone presents itself in the fluor spar of Wolsendorf, in Bavaria. This mineral has a peculiar smell, due to antozone, which Schoenbein found in the proportion of $\frac{1}{5000}$ of the weight of the spar, because five grammes, when rubbed with water, yielded 2.125 milligrammes of peroxide of hydrogen. Since antozone is contained in powder-smoke, it may be surmised that the copious rains which follow great battles are due, in a measure, to this body, the decomposition of the cloud of antozone-water being either a cause or an effect of the electrical excitement in the atmosphere.

Having prepared antozone from an antozonide, Schoenbein sought to obtain ozone from an ozonide, and selected permanganate of potassa for that purpose. Bertazzi had already (Cimento ii, 291) shown that by the action of dilute sulphuric acid, at a low temperature, upon this salt, a gas was generated which had the properties of ozone. Schoenbein, upon a further investigation of the subject, found that peroxide of barium projected into the olive-green solution of permanganate of potassa, and oil of vitriol, of 1.85 specific gravity, evolves a gas which has the smell and chemical properties of ozone. It acts strongly upon the mucous membrane, polarizes platinum negatively with great power, and destroys organic coloring matter and pyrogallie acid at the ordinary temperature. R. Boettger, in calling attention to this experiment, states that he had two years previously described the effect of oil of vitriol and permanganate of potassa in producing a long-continued evolution of ozone. He considers the addition of peroxide of barium superfluous, and, for the development of ozone, adds two parts of dry powdered permanganate of potassa to three of hydrate of sulphuric acid in a bottle. By this reaction a strong ozone smell is at once perceived, and all of the characters of the gas may be established by the proper reagents.

Schoenbein has determined that antozone has a density less than hydrogen, and that it liquefies at a pressure of 150 atmospheres. Ozone and antozone,

exposed to the dark rays of the spectrum, unite, with explosion, and yield ordinary oxygen.

Schoenbein considers that oxygen undergoes chemical polarization in the body when respired, and accounts thus for the rapid changes which take place in the tissues. He has found peroxide of hydrogen in the urine, and has discovered that the blood corpuscles instantly decompose this compound. He has given the following test for the peroxide of hydrogen. To water, supposed to contain the peroxide, he adds one or two drops of a solution of a salt of bismuth, nickel, cobalt, thallium, &c., and then just enough of potassa to precipitate the hydrated oxide of the metal. He then adds a little iodide of potassium and starch, and lastly one or two drops of acetic or dilute sulphuric acid. If the merest trace of peroxide of hydrogen be present, the liquid is instantly colored blue.

The following is Schoenbein's method of determining quantitatively the decomposition of oxygen into ozone and antozone. During the slow oxidation of metals, according to this chemist, the oxygen is chemically polarized; one of its atoms (ozone) unites with the metal or oxidizable matter, while the other atom (antozone) combines with water to form peroxide of hydrogen. Schoenbein agitates an amalgam containing five per cent. of lead, with very dilute sulphuric acid of known strength, in a large bottle partially filled with air or oxygen. After a few moments of agitation, a quantity of sulphate of lead is produced, and peroxide of hydrogen is found in the acidulated water. He ascertains the oxygen which has combined with the lead, by determining the amount of uncombined acid, thus calculating the sulphate of lead formed, and consequently its oxygen. He determines the peroxide of hydrogen in another portion of the water by a standard solution of permanganate of potassa, and finds the quantity of oxygen in this peroxide to be very nearly the same as that contained in the oxide of lead.

Different chemists have determined the diminution of volume experienced by air or oxygen during ozonization.

Andrews and Tait placed pure dry oxygen in a tube and discharged electricity through the gas. With still discharges a diminution took place, which was at first rapid and then slow until a maximum was reached, yielding a diminution equal to $\frac{1}{12}$ of the original volume. When, now, a few sparks were passed through the gas it expanded $\frac{3}{4}$ of the former diminution, but did not attain its original volume. With rapid or spark discharges, oxygen experiences a diminution of volume, although less than by still discharges. Oxygen, contracted by the formation of ozone, when left to itself at the ordinary temperature, expands again gradually. At 100° Centigrade it expands more rapidly, and at 270° it regains its original volume and loses all of the characteristics of ozone. At this temperature, therefore, ozone is destroyed. Andrews and Tait found that, by still discharges, oxygen cannot lose more than $\frac{1}{12}$ of its volume, unless the ozone be removed as fast as it is generated, in which case the diminution may proceed indefinitely. They determined 60 for the density of ozone compared with oxygen, which makes it six times lighter than lithium. They were unable to condense it to a liquid at ordinary pressures by a freezing mixture of solid carbonic acid and ether.

Ozone may be prepared for examination most readily by dropping, in small quantities, dry permanganate of potassa in a bottle containing a little oil of vitriol, or by placing a stick of phosphorus, scraped clean under water, in the bottom of a capacious vessel containing enough lukewarm water to half submerge the phosphorus. In either of these cases a slip of iodide of potassium starch-paper becomes instantly blue when immersed in the air of the vessel, and the different ozone reactions may be readily perceived by employing the appropriate tests. The gas may also be investigated with the above starch-paper in the neighborhood of a point upon the prime conductor of an elec-

trical machine, from which still discharges are issuing. It may be obtained by the inductive current of the Ruhmkorff coil, or by the electrolysis of water, using a powerful Bunsen or Grove battery, and employing gold or platina for the positive electrode, from which proceeds a current of oxygen, laden with ozone. The hydrogen gas, issuing from the negative electrode, possesses no odor of ozone, but this smell is perceived when the two gases are collected together. The antozone, formed here by the polarization of the oxygen, unites with the water to peroxide of hydrogen. If the water thus electrolyzed contain substances capable of union with oxygen, as hydrochloric, hydriodic acids, and their salts, also sulphurous acid, sulphuretted hydrogen, coal, iron filings, &c., or if the liquid or electrodes be heated, no ozone smell is perceived.

There is no process for obtaining pure and isolated ozone, although a constant current of air laden with this gas may be procured for a certain time by the action of sulphuric acid upon permanganate of potassa, or by passing moist air through a tube containing pure phosphorus, and washing the gas with water. The generation of ozone by the electric discharge is so slow that Baumert, by passing 500,000 sparks in an hour, obtained only enough of this gas to liberate one milligramme of iodine from its potassium salt.

Circumstances influence the production of ozone by the electrical discharge. Under the same conditions, sparks of 25 millimetres in length generate twice as much ozone as sparks of 4 to 5 millimetres long.

Employing hermetically sealed tubes of $\frac{8}{10}$ millimetres diameter and 70 millimetres long, $\frac{2}{3}$ of the oxygen can be converted into ozone; but by continuing the discharges the ozone diminishes, so that in 24 hours it equals only $\frac{1}{3}$ of the original oxygen.

By the electrolysis of water, containing $\frac{1}{10}$ of sulphuric acid, Baumert obtained only one milligramme of ozone in 150 litres of the mixed gases; but when the water contained chromic acid instead of sulphuric, he found the same quantity of ozone in 10 litres of the mixed gases.

Ozone is generated by means of phosphorus only in a moist air, containing oxygen at a medium temperature. When the atmosphere is deprived gradually of its oxygen, by means of ignited oxide of copper, the production of ozone diminishes, and ceases entirely when there is no longer any oxygen present.

Ozone is not formed in pure carbonic acid or hydrogen gases. With 1 volume of oxygen and 4 of carbonic acid, the formation of ozone is easy. In an explosive mixture of hydrogen and oxygen, the generation of ozone is powerful; the phosphorus shines vividly, and can acquire heat sufficient to kindle and explode the mixture of gases. In pure oxygen, at the ordinary pressure of the atmosphere, phosphorus, by the presence of water, does not produce ozone until the temperature is raised from 75.2° to 86° Fahrenheit. At this temperature the phosphorus begins to emit light, and the illumination and ozone generation are powerful at 96.8° Fahrenheit.

Oxygen expanded to four times its volume, by the air-pump, yields ozone, by phosphorus, at the ordinary temperature; but at 32° Fahrenheit there is no production of ozone. In dry air phosphorus generates ozone slowly, as the phosphorus soon becomes coated, which prevents the action of the air. There is a connexion between the shining of phosphorus and its generation of ozone, so that this production exists in proportion to the intensity of the illumination; but we are ignorant of the cause of this connexion.

If we well wash air ozonized by phosphorus and place in it a piece of carbonate of ammonia, so that the gas reacts alkaline, and wash the gas again, it still gives all of the characteristic reactions of ozone.

According to Schoenbein's experiments, 1,000 grammes of phosphorus are capable of converting 1,720 of oxygen into ozone. By another trial he gives 0.43 gramme as the yield of ozone by 1 gramme of phosphorus. By hanging silver leaf in a vitriol carboy filled with ozonized air, he could deozone the

same in four hours; and, by repeating the process for several weeks, he was able to prepare as much as 20 grammes of the peroxide of silver. Ozone results also from the slow oxidation of pure ether, effected by the means of a platinum spiral heated to redness and placed in the vapor of the ether. According to Schoenbein the combustion of hydrogen, carbide of hydrogen, and of kindred gases, produces ozone.

The odor of ozone is so powerful that air containing only one millionth of it has a decided smell of the gas. Ozonized air raised to the temperature of 482° to 572° Fahrenheit, is deprived instantly of this body.

A very characteristic action of ozone consists in its polarizing effects upon the metals, particularly upon platinum, gold, and, to a less extent, copper. An ozoniferous atmosphere behaves like one containing chlorine or bromine. If a slip of gold or platinum is immersed in an ozone atmosphere, it acquires a *negative* polarity in a few seconds. When such a slip is united with an ordinary one and the pair is plunged in acidulated water, a current is generated which acts powerfully upon the needle of the galvanometer. Antozone, also, polarizes platinum negatively, but less so than ozone.

In the preparation of ozone by phosphorus, an odor characterized as "garlic" is first perceived. Gold or platinum, immersed in such air, is polarized *positively*, and this condition may remain for a considerable time if the temperature be low. Presently, with a temperature of 53.6° to 60.8° Fahrenheit, the gas exchanges its "garlic" for an ozone smell; and, at the same time, the metal, after quickly passing Volta's point of indifference, acquires a *negative* polarity. The least moisture deposited upon the metal, also an elevated temperature, prevent, or, if present, destroy this polarization. It is also lost in the air gradually, and immediately in hydrogen gas, which even communicates a positive polarity.

Ozone is absorbed neither by water, caustic ammonia, nor baryta, sulphuric acid, or dry chloride of calcium.

Schoenbein attributes many of the reactions of oxidation by the "*nascent state*" of the gas to the presence of ozone.

Dr. Phipson has given many of such examples of polarization explanatory of the "*status nascens*" in a prize essay which is contained in the Smithsonian Report for 1862.

A paper saturated with a solution of iodine is quickly bleached in an ozone atmosphere; the product, however, does not react acid, and in contact with oxidizable bodies, such as sulphurous acid, sulphide of hydrogen, phosphorus, hydriodic acid, metals like zinc and tin, or protoxides like those of tin or lead, the paper becomes brown again from iodine.

Solutions of chlorine and bromine act in the same manner; and it is this fact, together with the chemical analogies existing between ozone and the halides, which led Schoenbein to assign to ozone a similar nature.

In the presence of strong bases, such as hydrates of lime or potassa, the nitrogen of the air may be oxidized to nitre by the action of ozone. Three thousand litres of ozonized air, agitated with milk of lime, furnish 5 grammes of saltpetre. Ozone liberates iodine from the iodide of potassium more freely in the sun than in the daylight; but when starch is present, the blue iodide of starch is bleached by the light. By renewed action of ozone it becomes blue again, and the bleaching and bluing may be repeated until the iodide of potassium is transformed completely into iodate of potassa; when ozone is no longer capable of producing the blue tinge. According to Baumert, the first effect of ozone upon this salt is the decomposition to caustic potassa and iodine, which react to form iodate of potassa and iodide of potassium. The ozone acts upon this iodide as before, until at length the halide is completely oxidized to iodate of potassa.

The yellow prussiate of potassa is converted quickly into the red prussiate

by ozone. A crystal of the former salt placed in an ozone atmosphere becomes gradually red, the color proceeding from the outside to the inside, and the solution of ferrocyanide of potassium experiences this change very readily when agitated with ozone.

The metals arsenic, antimony, iron, zinc, tin, lead, bismuth, silver, and mercury, are oxidized instantly by ozone, and deprive thereby any atmosphere containing that gas.

The metals are not oxidized with equal facility. Thus arsenic is oxidized much more readily than antimony, which affords an additional means of distinguishing between these bodies in judicial inquiries. An arsenic spot in a strong ozone atmosphere is converted instantly to arsenic acid, while an antimony mirror requires several days for its disappearance. Dry mercury, or that covered with water, does not absorb ozone; if the metal be merely moistened, it takes up ozone readily, becoming yellowish upon the surface.

Silver, in the state of leaf or sponge, absorbs ozone quickly, as has been stated already. This metal may be employed for separating ozone from ordinary oxygen.

The more readily oxidized metals, as protoxides of manganese, iron, tin, &c., as well as those which, like protoxides of silver and lead, are not so easily changed to a higher state of oxidation, are peroxidized by ozone.

A solution of the sulphate of the protoxide of manganese is browned instantly in ozone from the above cause, and, according to Schoenbein, this reaction is perceptible in a dilute solution of sulphate of zinc, which contains as an impurity only $\frac{1}{1000}$ of manganese. If hydrated oxide of lead be spread upon paper, or if basic acetate of lead be employed, ozone will communicate to the paper first a yellow, then a red, and finally a brown coloration from the peroxidation.

If the lead paper be blackened by means of sulphide of hydrogen, it may be bleached in ozone, which is due to the production of the white sulphate of lead.

Organic bodies are very readily oxidized in ozone, as shown by the experiments of Schoenbein, Baumert, Gorup von Besanez, &c. Thus wood, straw, cork, starch, humus, vegetable colors, caoutchouc—pure and vulcanized—the fats and fatty acids, alcohol, albumen, blood, &c., have been found to be all acted upon by this agent. Ozone bleaches litmus without first reddening it. Certain fungi become blue in the air, and the cut surface of an apple becomes brown by the action of ozone.

Gum guaiacum, which becomes gradually blue in the air, owes this change to ozone, as was first shown by Schoenbein, who employed this substance as a reagent for ozone. To prepare guaiacum papers, one part of the gum is dissolved in thirty parts of 90 per cent. alcohol. One gramme of ordinary alcohol is charged with a few drops of this solution, and the paper slips are dipped therein and dried. The papers are blue rapidly in an ozone atmosphere. They lose this color when exposed to the air, but regain it in ozone, and the process may be repeated until the guaiacum is fully oxidized. Certain metals and other bodies, especially nitrous acid, chlorine, bromine, peroxides of manganese, and lead, &c., will blue guaiacum tincture.

The following is Schoenbein's method of determining ozone quantitatively in a mixture from its bleaching effect upon the solution of indigo: The ordinary solution is diluted with sufficient water to be just opaque blue. One hundred grammes of this solution receive an equal weight of hydrochloric acid, and are then boiled. The heated liquid is treated with a solution containing $\frac{1}{100}$ of chlorate of potassa until the blue color is exchanged for a brownish yellow. If, now, for the destruction of the 100 grammes of indigo solution, 100 milligrammes of chlorate of potassa (which contain 39 milligrammes

of oxygen) were employed, then 1 milligramme of oxygen would destroy $\frac{1.00}{2.9} = 2.564$ grammes of indigo solution. Now, to this last quantity of the original indigo solution, containing hydrochloric acid, enough water must be added to dilute it to 10 grammes,* in order to obtain a normal solution of which 10 grammes will represent 1 milligramme of oxygen or ozone. One part of the above normal solution may be further diluted with 9 parts of water to yield $\frac{1}{10}$ normal test, in which 10 grammes will indicate $\frac{1}{10}$ milligrammes of ozone.

The analysis is performed as follows, for example, upon a bottle of air ozonized by phosphorus: A little of the normal indigo solution is agitated with the air in the bottle for a few minutes, and the air is then tested for ozone by iodide of potassium starch, and the process is repeated until no ozone is indicated even by a slightly elevated temperature. Then, for every 10 grammes of the normal indigo solution employed, 1 milligramme of ozone is present, and for every 10 grammes of the $\frac{1}{10}$ normal solution, $\frac{1}{10}$ of a milligramme of ozone has been found.

Schoenbein discovered the remarkable bleaching properties upon indigo and other plant colors of certain bodies which appear to absorb ozone, without combining with it, and thus are in a position to yield the ozone again to other substances. These bodies have been called "*ozone carriers*." They are oil of turpentine, linseed oil, oil of lemons, tartaric and citric acids, ether, platinum sponge and black, powder of silver, gold, and platinum, also metallic mercury. These substances, shaken with solutions of indigo, litmus, cochenille, &c., discharge the color; with tincture of guaiacum they yield a blue tinge, and give the same color with iodide of potassium starch. One of the most remarkable of the ozone carriers is the blood corpuscle. Ozonized oil of turpentine, shaken with indigo solution, bleaches it after a while, but if blood corpuscles are added, the decoloration is instantaneous. Platinum black is also very active in its bleaching effects.

One of the best known ozone carriers is the oil of turpentine. If a bottle be $\frac{1}{4}$ filled with this body, exposed to the sun, and frequently shaken with air, removing the stopper from time to time to renew the air, the oil is speedily laden with ozone. After a time the oxidizing or bleaching effect of this oil is lost, probably from its ozone entering into combination with it. Its bleaching effect may be ascertained quantitatively by means of a solution of indigo. Schoenbein prepared an oil of which 1 gramme possessed the same bleaching power as 2 grammes of the best bleaching powder, (hypochlorite of lime.) The ozonized oil bleaches most rapidly when warm, but its absolute decolorizing power is then less. All turpentine kept with access of air becomes ozonized, as may be seen from the bleached and corroded corks employed in closing the vessels containing it. Upon the animal organism ozonized oil of turpentine acts more energetically than oil not ozonized. According to Seitz, 5 drops of ozonized oil throws into convulsions and kills a frog and destroys other small animals, while 20 drops of the pure oil produce no such effect. Not long since a statement prevailed that the disease called painter's colic is due, not to the lead absorbed, but to the oil of turpentine. If this be so, the ozonization of the turpentine may be the active agent for mischief, although the lead may also be hurtful.

The existence of ozone in the atmosphere has been known since the discovery, of the body; but the conditions which govern its presence, as well as the actual quantity of the gas, are yet undetermined. This arises from the small amount of ozone in the air, from the readiness with which this active oxidant is destroyed by the presence of bodies upon which it may act, and also for the want of a re-

* Hence, in this case, $10 - 2.564 = 7.436$ water will be needed.

liable quantitative test. The largest proportion with which the air has been artificially loaded with this substance amounts to $\frac{1}{1300}$ of its volume.

Ozone may be determined quantitatively by ascertaining the amount of iodine liberated from iodide of potassium; by determining the quantity of peroxide of silver which it produces; or by finding the proportion of indigo solution which it decolorizes. But this kind of test has never been applied to a great extent in determining the atmospheric ozone in long series of observations, owing to the difficulty and labor of applying it.

A large volume of air brought slowly to act upon a small proportion of the reagent is necessary for this purpose. In aspirating twenty-four litres of external air during a period of two and a half hours, concentrating its action upon a circle $\frac{1}{32}$ of an inch in diameter on a delicate iodide of potassium starch paper, I was unable to detect the slightest ozone reaction, although a slip of similar paper exposed all day to the free atmosphere was colored sensibly.

The ordinary mode of observing ozone in the atmosphere consists in ascertaining the amount of color produced upon paper containing iodide of potassium and starch, using precautions against the bleaching effect of the light upon the iodide of starch developed by the ozone. A scale of shades of color is employed for determining, by comparison, the proportion of the gas in question present in the atmosphere. Boehm found that this test, prepared from the same recipe by different persons, gave varied results. According to Osann's formula, thirty-two grains of starch are rubbed in a mortar, with the same quantity of cold water; three grains of iodide of potassium are then dissolved in four ounces of boiling water, and the solution is added to the starch and well incorporated with it. After boiling once more, the test is cooled and placed in a bottle for use. When reagent paper is required, slips of Swedish filtering paper are shaken up with the starch liquid, and then dried. This paper is instantly colored of a deep shade of blue when exposed to the ozonized air of a bottle containing phosphorus and a little water. Exposed during the night to the atmosphere, the coloration by ozone is very decided.

In the ordinary atmospheric ozone observations the velocity of the air-current which traverses the reagent paper influences the result by bringing a greater proportion of ozone upon the test in a given time. The determinations which have been hitherto made are very vague, unsatisfactory, and yield but rude comparative results as to the subject in question.

Notwithstanding this difficulty, theories have not been wanting as to the influence of ozone upon the health. The oxidizing action of ozone upon organic substances as shown by Gorup von Besanez, the phenomena of ozone carriers, such as oil of turpentine, platinum sponge, and the *blood corpuscles*, have facilitated the formation of such theories.

Dr. Smallwood, in a long series of observations upon the atmosphere of Canada during the prevalence of the cholera and at other times, favored the inference of a deficiency of ozone during the epidemic.

Dr. Moffatt concluded, from a large number of observations in England, that the ozone in the atmosphere plays an important part in controlling or preventing epidemics, which it effects by removing the infectious matter from the air. During the prevalence of the cholera at Newcastle, in 1853, this gas was at its minimum. From August 24 to September 11, 1854, when the disease was at its height in London, ozone was observed only once, and then in but small quantity. On the 10th September a south wind prevailed, by which the ozone was found to increase, and the cholera cases diminished. During the Crimean war the surgeons of the French army established the following facts:

1. In proportion as the ozonoscopic papers were more colored in the air, the more numerous were the sick taken to each of the hospitals.

2. When the temperature was higher, there were fewer sick and fewer deaths.

3. At the three observatories the curves designating the proportion of ozone were essentially the same.

4. The curves for temperature were also identical.

5. At observatory No. 1 the quantity of ozone was *inversely* proportional to the number of deaths, while in observatory No. 2 this proportion was a *direct* one.

Bineau detected ozone but seldom in the air of Lyons, although he observed it always in the air of the neighboring country. He attributes the deficiency in the city to the action of organic matter in the air.

Pless and Pierre discovered 0.02 milligramme of ozone in 255 litres of atmospheric air.

Zenger found in twelve experiments from 0.002 to 0.01 milligramme of this body in 100 litres of air.

R. Angus Smith ascertained that the air of Manchester did not react with ozonoscopic paper, nor was there any reaction in the country when the air had first traversed the city; which he attributes to the absorption of ozone by the products of combustion, (autozone?) arising from the large amount of coal burned in the city.

C. Kosmann ascertained that in Strasburg, and at a short distance from the city, there was more ozone in the air of the country than in that of the city. In the city, the ozone maximum occurred in the daytime; in the country, at night. He found also, by the action upon Schoenbein's test paper, that the green portions of all plants exhale ozone.

Mr. Carey Lea discovered that the growth of plants is retarded in an atmosphere strongly impregnated with ozone.

A. Poey found that in the city of Havana the ozone reaction diminished with the elevation, while in the country the reverse was observed. He also discovered that the moisture of the atmosphere influenced the amount of ozone.

I ascertained that the air of the public grounds in Washington yielded, at night, abundant evidence of ozone, while the atmosphere of the streets of the city, observed at the same time, indicated an absence of this gas.

Dr. W. B. Rogers found that the air passing over Boston was deprived of its ozone by the emanations from the city.

M. Hozeau, of Rouen, inferred, from a series of observations which extended over four years, that the atmospheric ozone is least in February, begins to increase in March, and reaches its maximum in May and June, after which month it diminishes to its minimum in February.

J. Boehm has given the results of four years of regular observations of ozone, made in the city and environs of Prague. His ozonoscopic paper was observed and changed at 7 a. m. and 7 p. m., the proportion of ozone being determined by the depth of shade of the color produced. He found that the ozone bears no relation to the relative humidity, rain or thunder storms, clouds, &c., but is intimately connected with the force and direction of the wind, which was generally from the west when the phenomenon of color was observed. The reason of this fact is the relative position of the observatory to the city of Prague, so that all easterly winds passed over a thickly-settled portion of the town, by the emanations of which they were deprived of their ozone.

In the country and suburbs, Boehm found ozone constantly present. Without expressing a decided opinion upon the relation of ozone to health, this physicist calls attention to the fact that in Koenigstadt, a place not particularly noted for its salubrity, he obtained as decided reactions of ozone as upon the healthiest mountain, and that the coloration of the test paper is more decided in Vienna, a city noted for its lung and typhoid fevers, than in Prague, which is ranked justly with the healthiest towns.

From what is known at present respecting "autozone," it would seem that this body plays an important part in depriving the atmosphere of ozone.

In judging from the reaction upon iodide of potassium starch paper, ozone is always in the free atmosphere in variable, but small, quantity. Such test papers are not blued when closed in a bottle, and scarcely so, if at all, in a room. By exposure to the external atmosphere the effect upon them is extremely variable. Sometimes in cities it is imperceptible. According to Osann, the coloration is greater by night than by day, and is more decided towards sunrise, at the time when the atmospheric moisture is precipitated. It is greater in winter than in summer, stronger with clouded than with clear sky, and is especially powerful with snow clouds. Every flake of snow falling upon the test paper produces a blue stain. By atmospheric electrical discharges ozone is, as might be expected, very prevalent. Schoenbein calls attention to the fact that the odor in the neighborhood of places struck by lightning is exactly that of ozone.

The whole subject of ozone, whether in its physical or physiological relations, is intensely interesting, and promises, when understood, to be the means of solving many problems in the sciences now so difficult to be comprehended. No field of research appears to promise so rich a harvest to the skilled and patient observer.







